Development of Process Optimization Strategies, Models, and Chemical Databases for On-Line Coating of Float Glass

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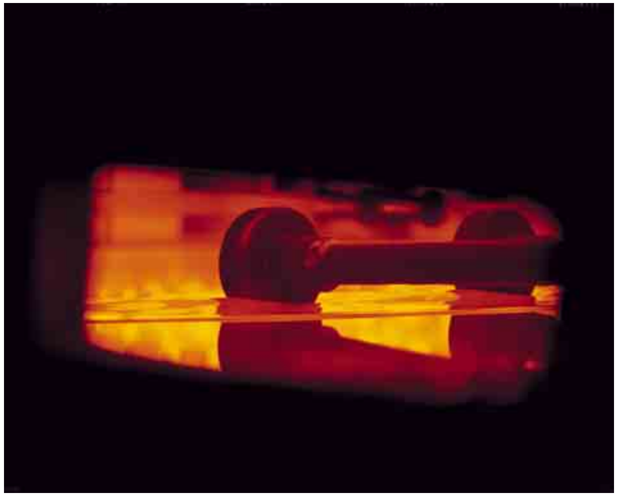
Atmospheric Pressure Chemical Vapor Deposition (APCVD) In The Glass Industry

Goals: Double the efficiency of tin precursor utilization and reduce coating defects related to thickness

Challenges:
- Very complex process
- High process development costs
- Knowledge base required to develop process models is absent

Benefits: Doubling efficiency of precursor use will save $13 M/year in waste disposal costs, while reductions in coating defects could save 4.5 x 10^{10} BTU/year to remelt glass

FY05 Activities: CRADA with PPG extended to 12/04 to evaluate production and licensing potential of IP.



Participants: Sandia National Laboratories, PPG Industries, TNO

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Barrier-Pathway Approach

Barriers

- Lack of chemical data needed for process models
- No reliable measurements of film growth kinetics
- Testbed needed to validate models and evaluate optimization strategies

Pathways

- Theory, modeling, and experiments (SNL, TNO)
- Lab reactor constructed to provide required data
- Pilot-scale experiments and full-scale plant trials conducted by PPG

Critical Metrics

- Model predictions validated by experiment
- Successful plant trials
- 2X increase in precursor utilization efficiency
- 2X reduction in waste glass due to coating defects

Benefits (est.)*	2020
Energy Savings	**350 billion Btu**
Savings due to reduced solid waste	**$200 million**

*2005 – 2020 est. cumulative total

Project Tasks

- **Task 1: Deposition Mechanism Development (SNL)**
  - Thermodynamic Data
  - Gas-Phase Chemistry
  - Surface Mechanism
  - Defect Formation
- **Task 2: Reaction Rate Measurements (SNL, TNO)**
  - Gas Phase Reactions
  - Surface Reactions
- **Task 3: On-line Coater Effluent Analysis (SNL, PPG)**
- **Task 4: CFD Modeling of Coating Reactors (SNL, PPG)**
- **Task 5: Deposition Experiments (SNL, PPG)**
  - Model Validation
  - Defect Analysis
- **Task 6: Validation of Optimization Strategies (SNL, PPG)**

This project successfully met its original goals set out in the original proposal

- **Identify process modifications that will double the efficiency of reactant use to reduce waste emissions and purchases of raw materials**
  - **Strategies identified through modeling now undergoing full-scale testing**
- **Develop computational models to predict defects due to thickness nonuniformity and haze**
  - **Models transferred to PPG for use in full-scale simulation of coating operations; models available for use by the industry**
- **Generate a database of fundamental thermodynamic and kinetic information for APCVD**
  - **Thermodynamic data now available on the web: www.ca.sandia.gov/HiTempThermo/index.html**
- **Provide enhanced understanding of the underlying chemical reactions that control APCVD to enable development of coatings for other glass types, such as containers**
  - **8 Publications in reviewed journals or proceedings, 12 presentations**

Tin Oxide Deposition Kinetics and Model Development

(Tasks 1, 2, & 5)

Objectives:

- **Develop validated process model**
- **Generate thermodynamic and kinetic data for chemical precursors needed for modeling**
- **Provide enhanced understanding of underlying chemistry and physics of APCVD**

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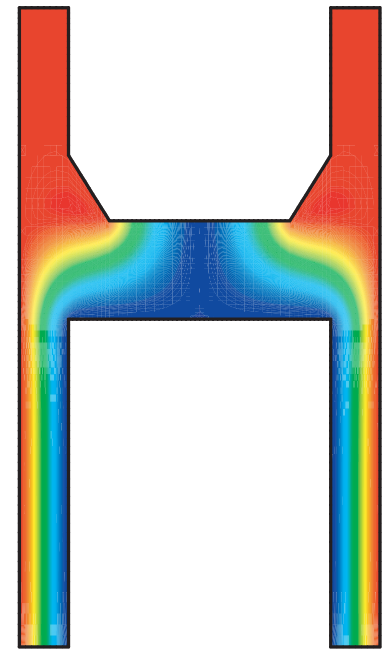
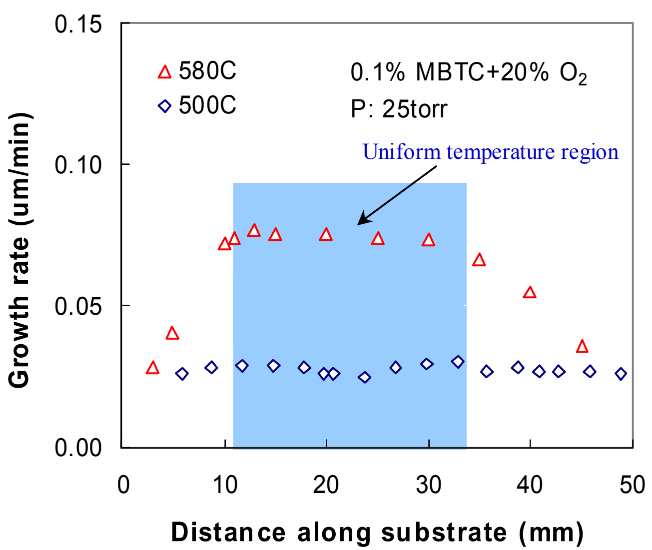
New Sandia reactor provides the flexible testbed required to develop useful models of on-line coating

- **Broad range of accessible deposition conditions**
- **Uniform deposition due to is well behaved flow**
- **Simplified modeling due to 1-D flow environment**

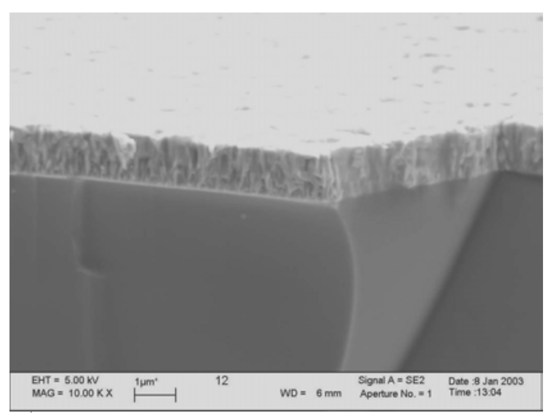
Streamlines





Temperature: ± 8 K
Growth rate variation:

- 500 ° C: ± 5.8%
- 580 ° C: ± 3.8%



PPG's pilot-scale coater provides a realistic environment for model testing and validation

- **Pilot scale coater has been modified to coat stationary substrates**
  - **Allows steady-state deposition and analysis of exhaust gases**
  - **Stationary heater installed directly under coater face**
  - **New coater face for heat transfer fluid channels for temperature control**
  - **Heat transfer fluid circulation system installed**

Side view of pilot-scale coater interior

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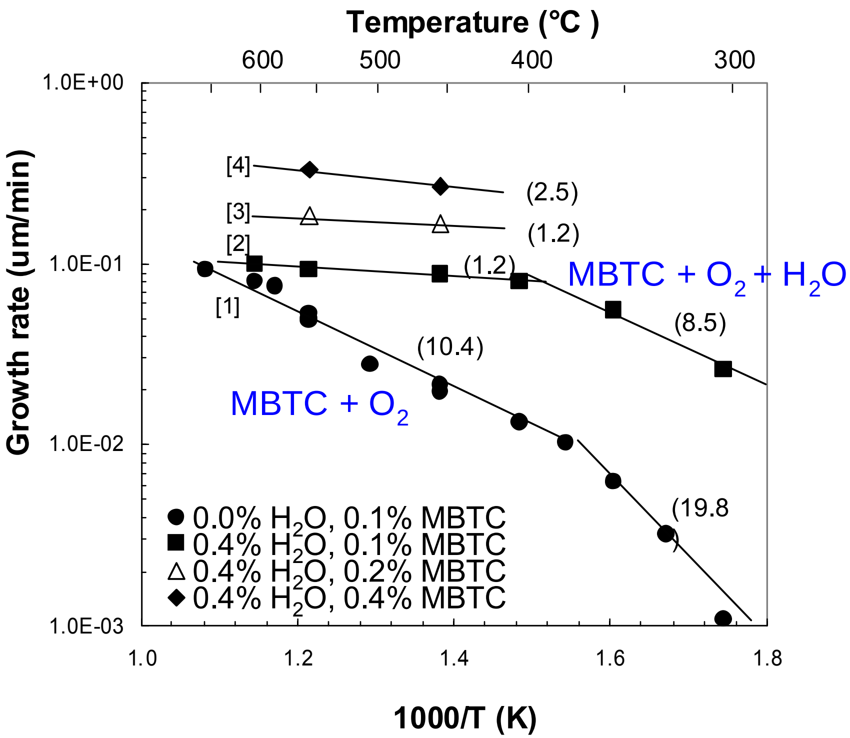
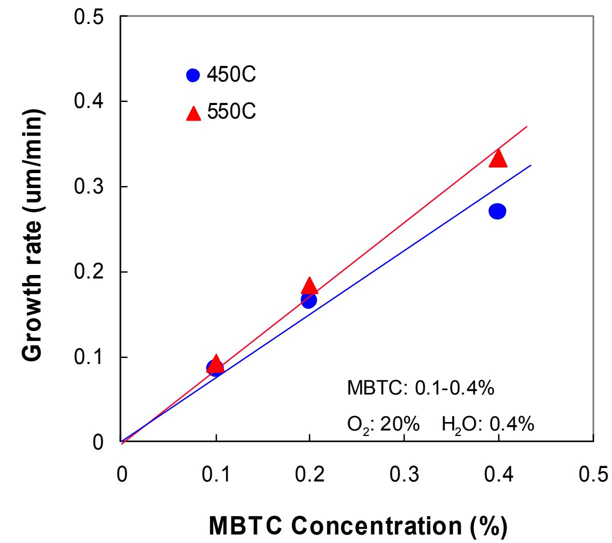
The kinetics of tin oxide deposition were fully characterized as part of this project



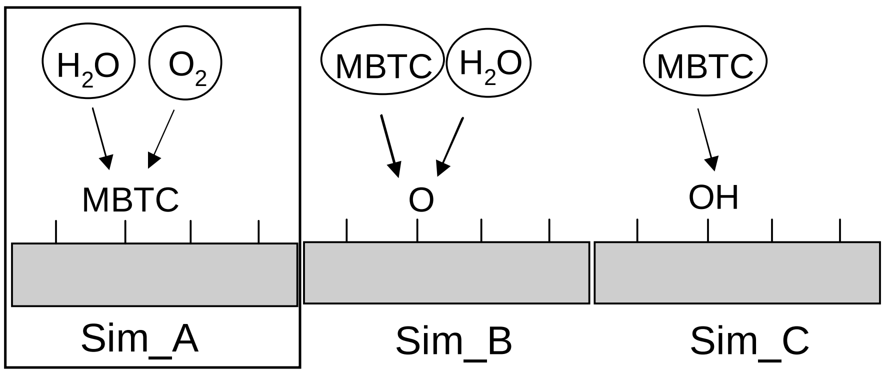
- **Effect of H_2O addition**
  - Decreases the activation energy
  - Changes the rate-controlling step:
    T > 400 °C : Mass transfer
    T < 400 °C : Kinetic
- **Which species govern the mass transfer? Two possibilities:**
  1) MBTC itself to the surface
  2) Intermediates produced by rapid MBTC reaction in the gas phase (MBTC:H_2O complex)

Mass transfer limiting region

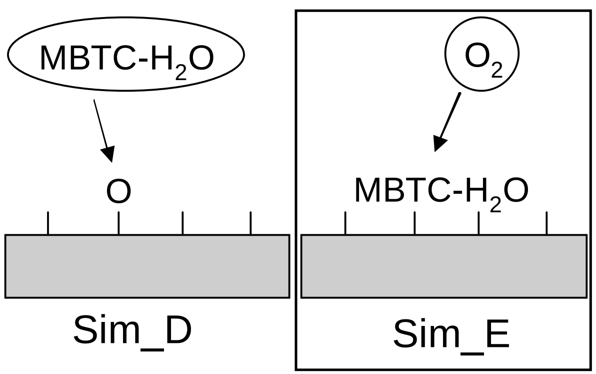


Several possible mechanisms exist for deposition from MBTC + O_2 + H_2O mixtures

No gas-phase reactions

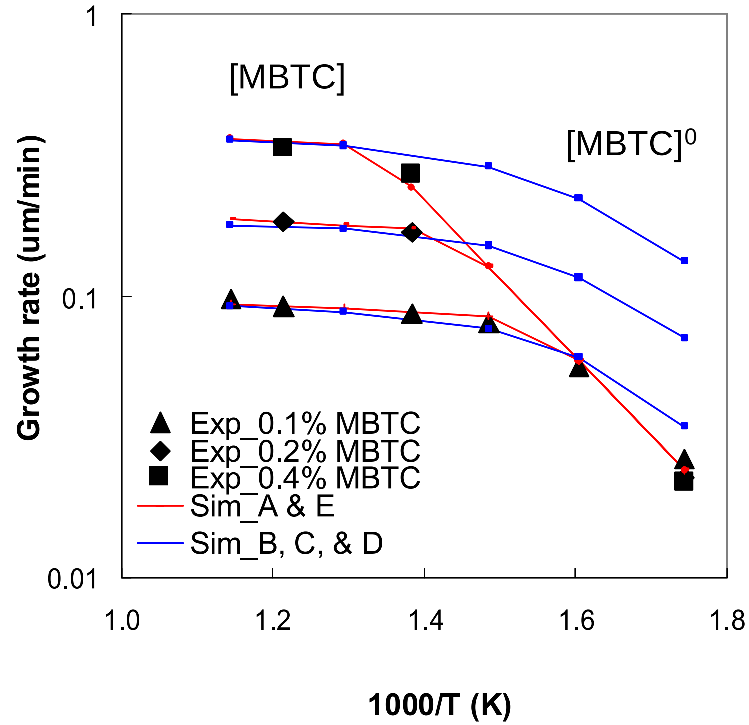


Gas phase reactions



SPIN simulation

0.1-0.4%MBTC + 20%O_2 + 0.4%H_2O, 25Torr



Sim_A and E are in good agreement with experimental data.

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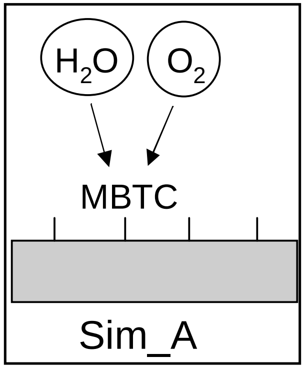
Comparison of Sim_A & Sim_E for MBTC + O_2 + H_2O reaction



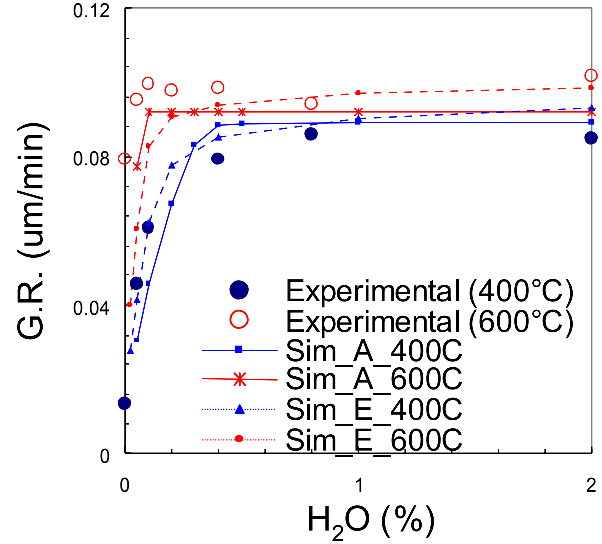
$C_4H_9SnCl_3$ + _(s) → $C_4H_9SnCl_3(s)$ st. coef.=1

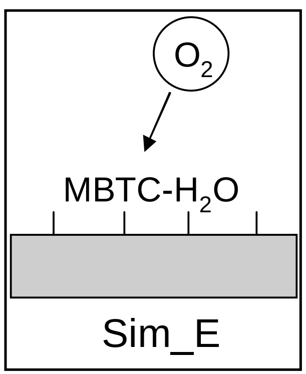
_(s): open site on surface

$$C_4H_9SnCl_3(s) + 1/2O_2 + H_2O \xrightarrow{k_s} SnO_2(B) + 3HCl + 2C_2H_4 + OS(s)$$

$$k_s = 1.5E16\ Exp(-12000 / RT)$$

$$GR \propto k_s\,[MBTC][O_2]^{1.12}[H_2O]^{0.5}$$





$$C_4H_9SnCl_3 + H_2O \xrightarrow{k_g} [C_4H_9SnCl_3{:}H_2O]$$

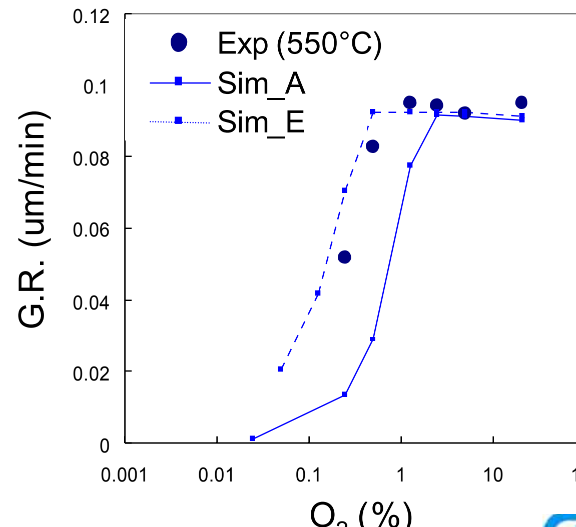
$$k_g = 4E14\ Exp(-10000 / RT)$$

$[C_4H_9SnCl_3{:}H_2O]$ + _(s) $\xrightarrow{k_s}$ $[C_4H_9SnCl_3{:}H_2O](s)$

$$[C_4H_9SnCl_3{:}H_2O](s) + 1/2O_2 \rightarrow SnO_2(B) + 3HCl + 2C_2H_4 + OS(s)$$

$$k_s = 1E10\ Exp(-13700 / RT)$$

$$GR \propto k_s\,[MBTC][O_2]^{0.76}$$



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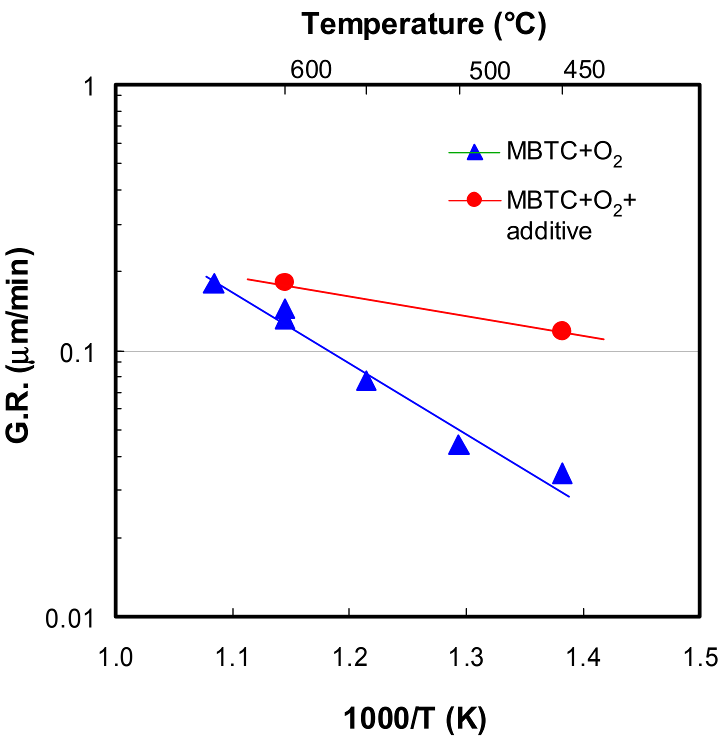
Preliminary experiments suggest that certain additives can accelerate tin oxide growth rates

- **Experiments in SNL reactor shows significant increases in growth rate**
- **MBTC conversion efficiency also increases**
- **Confirms predictions of kinetic model of MBTC oxidation**
- **SNL and PPG extended their CRADA to 12/04 to explore this further**
- **We are requesting additional funds from OIT to pursue this aspect of the project**



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CFD Modeling of Pilot-Scale Coater Deposition Experiments

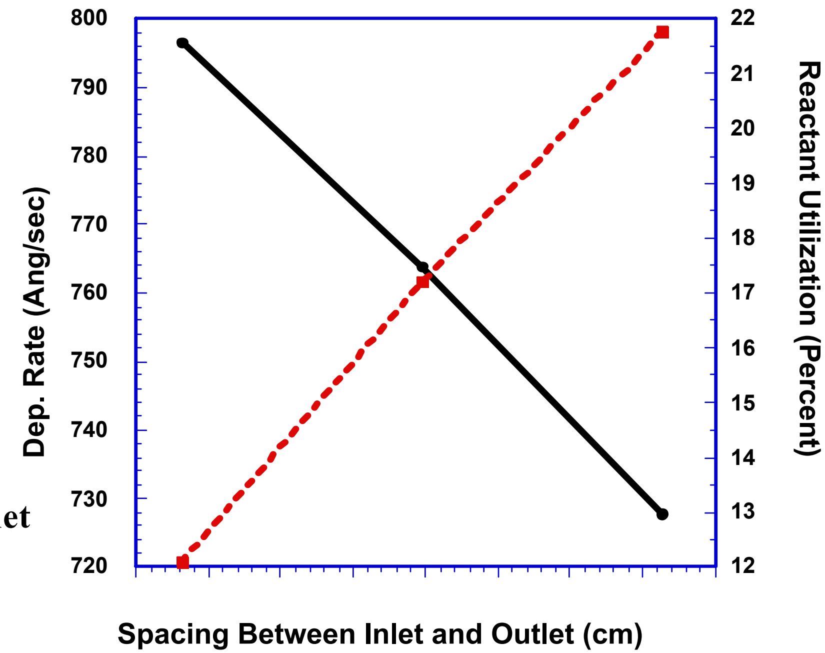
(Task 4)

<u>Objective</u>:

Develop validated process model effective for realistic coater designs

Task 4 FY03-04 accomplishments

- Transferred two deposition models to PPG for their use
  - Surface-only mechanism for MBTC + O_2 + H_2O
  - Surface + Gas-phase MBTC + O_2 + H_2O
- Advised PPG on selection of CFD modeling package
- Simulated PPG pilot-scale reactor to full-scale testing of optimization strategies
  - Inlet/Outlet spacing
  - Water concentration



Effect of Spacing between Coater Inlet and Outlet On Deposition Rate and Utilization

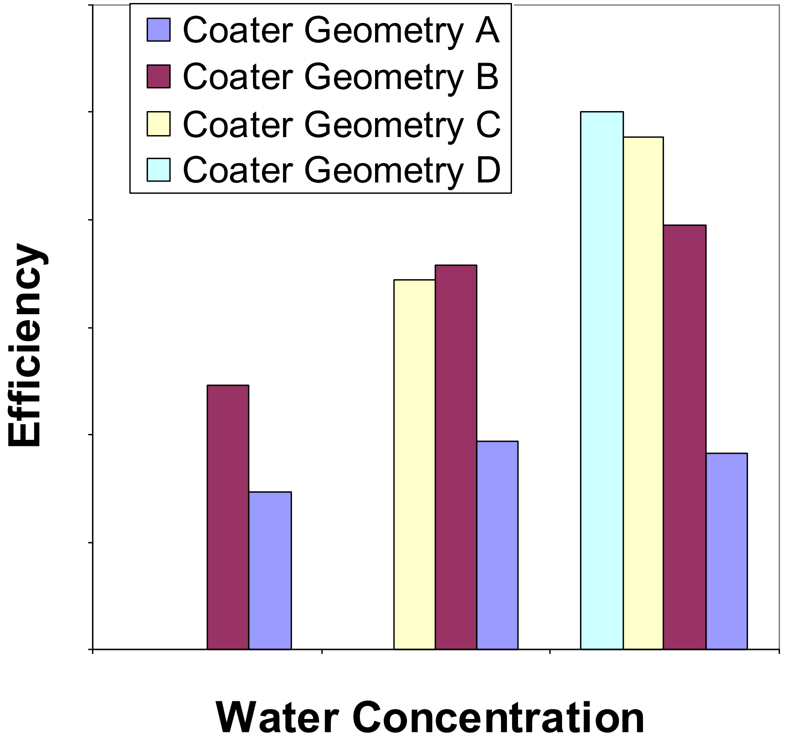
Optimization Strategies
(Task 6)

<u>Objectives</u>:

- **Identify modified/new APCVD coater designs that double the efficiency of reactant utilization**
- **Develop strategies to reduce coating defects, particularly non-uniform coating thickness**

Full Scale Plant Trials Conducted to Explore Maximum Efficiency of Precursor Utilization

- **Full scale plant trials were completed in October 2003 varying:**
  - **coater geometry**
  - **water concentration**
- **Under the most extreme conditions tested, the efficiency was > 3X the efficiency under standard conditions.**
- **Although the most extreme conditions are not feasible for PPG manufacturing, practical manufacturing conditions are projected to have an efficiency range of 1.5X to 2.5X the efficiency at standard conditions. Actual efficiencies will be determined after product qualification.**
- **The projected results are expected to meet the primary objective of the project (2X increase in efficiency of precursor usage)**



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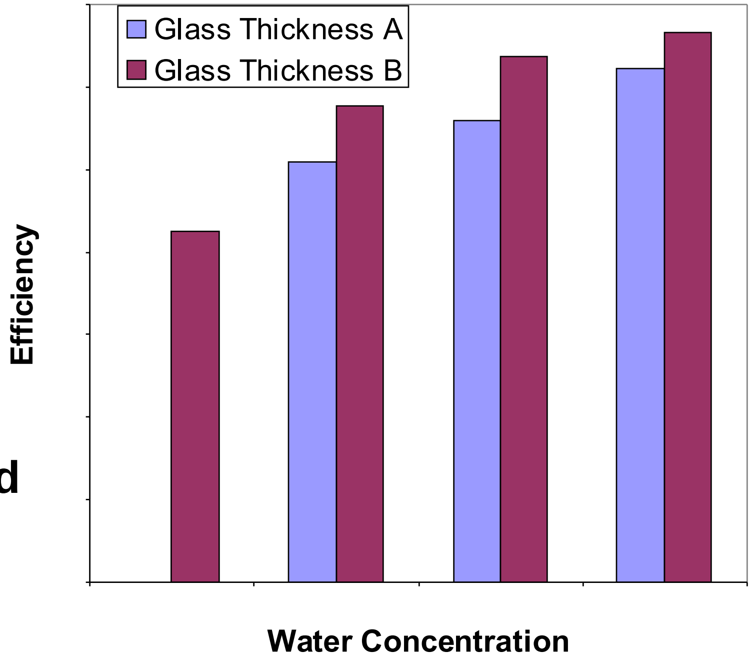
PPG Product Qualification

- Before new coating conditions are implemented during production, experiments simulating production must be conducted and samples must be analyzed and tested to assure coating quality.
- Coating qualities analyzed and tested
  - Sheet Resistance
  - Haze
  - Color Uniformity
  - Durability
- Product Qualification may limit the achievable coating efficiency

Full Scale Plant Trials Conducted to Verify Coating Quality for Implementation

- **Full scale plant trials were conducted in April 2004 on one glass thickness using increased water concentration and full coating stack**
- **Increasing water concentration increased efficiency by 20% over standard conditions**
- **Analysis and testing of samples is underway, but not yet complete**

- **Full scale plant trials were conducted in June 2004 on a second glass thickness using increased water concentration and full coating stack**
- **Increasing water concentration increased efficiency by 50% over standard conditions**
- **Analysis and testing of samples is just starting.**



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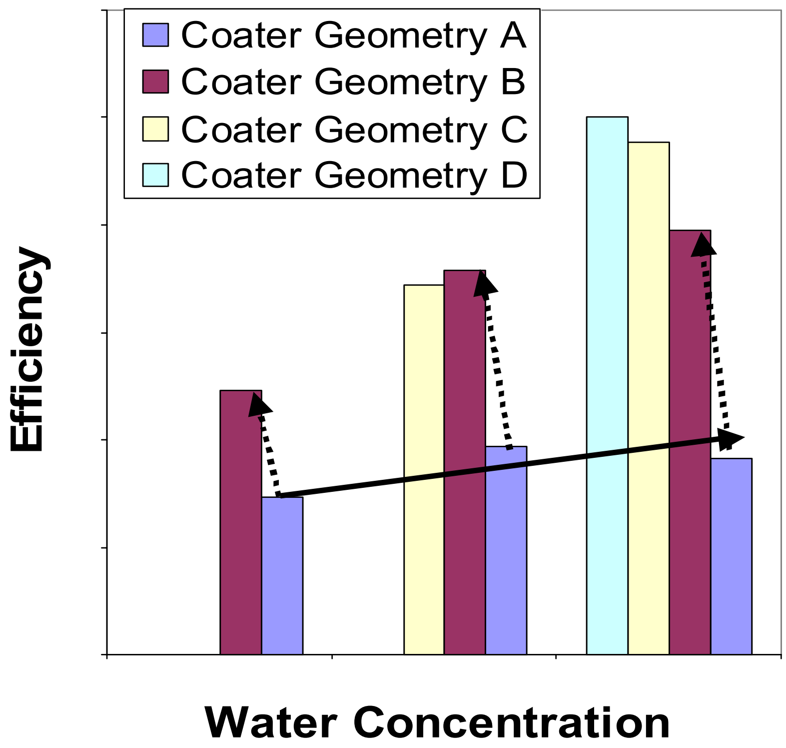
Future Trials and Implementation

- **Additional trials are on-going to verify the quality of coating using increased water concentration on all glass thicknesses.**
- **Trials will vary:**
  - **coater geometry with and without increased water**
  - **all glass thicknesses to verify coating quality with these conditions**
- **Implementation of new coating conditions will occur on each glass thickness as soon as coating quality has been ascertained to be good.**



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Significance to glass industry

- Optimization strategies are being tested on a full-scale manufacturing line to determine achievable efficiencies based on product qualification
- MBTC is a commonly used precursor in flat- and container-glass production
  - Film growth models developed here can easily be extended to other manufacturing processes using this precursor
  - Models are sufficiently robust to cover a wide range of process conditions
- Flow modeling demonstrates that useful insight can be obtained without the need for full-scale CFD.
  - Process engineers using cost-effective, lower-dimensional modeling software can identify strategies to improve efficiency; full-scale CFD model is probably not necessary in most cases
- The use of additives to accelerate conversion and growth rates can be extended across the industry
  - Concept has commercialization potential
  - CRADA extended to explore this